ACCURACY OF THE IOS APPROXIMATION FOR HIGHLY INELASTIC R–T COLLISIONAL ENERGY TRANSFER. CO–Ar ☆

Sally CHAPMAN
Barnard College, New York, New York 10027, USA

and

Sheldon GREEN
NASA Goddard Institute for Space Studies, New York, New York 10025, USA

Received 18 July 1984; in final form 28 September 1984

Rate constants for rotational excitation of CO by collisions with Ar atoms have been computed within the infinite order sudden (IOS) approximation and compared with values from exact classical trajectories. For CO–Ar, as for CO–He, accurate values for $R(0 \rightarrow j)$ – at least for small and intermediate j – may be obtained by taking the geometric average of rates computed assuming the IOS energy is the initial energy for upward $0 \rightarrow j$ transitions and the initial energy for downward $j \rightarrow 0$ transitions. However, especially for higher j, it appears preferable to interpret the IOS energy as the final kinetic energy. The best overall results are probably obtained by averaging rates computed assuming the IOS energy is the final energy for upward transitions and the final energy for downward transitions.

1. Introduction

Of the various theoretical methods available to treat rotational excitation in molecular collisions, the infinite order sudden (IOS) approximation is probably the most powerful. Besides finding application in rotational relaxation problems, it greatly simplifies studies of vibrational relaxation [1]. Furthermore, scaling relationships that were first derived within the context of this approximation appear to be extremely powerful [2–4]. It is therefore of considerable interest to document the accuracy and range of validity of the IOS approximation.

Since rotational energy spacings are ignored compared to the kinetic energy in this method, one expects the IOS approximation to be poor when only a few rotational levels are energetically accessible (see, e.g. ref. [5]) but in that case more accurate methods, such as the coupled states approximation are often feasible. In the opposite case where many levels are energetically accessible one expects the IOS method to be good but verification of this expectation has been hampered by the difficulty of obtaining accurate values in this case against which to compare.

In a recent paper [6] we used classical trajectory methods – which are also expected to be accurate when many quantum states are populated – to study the accuracy of the IOS approximation for CO–He collisions. As expected, and as had been documented previously [5], the IOS method does provide a good description for this system for collisions in which the inelasticity is fairly small (i.e. small changes in the rotational quantum number). We showed in ref. [6] that one can obtain accurate results for this system even for highly inelastic collisions, but in that case it is necessary to interpret the meaning of the IOS kinetic energy with some care.

We present here a similar study of CO–Ar collisions. This system is a less favorable cae for the IOS approximation. Because of the larger reduced mass the collision velocity is slower compared with the rotational period, and the collision is therefore less sudden or

☆ Work supported in part by NASA grant NSG 7105.

0 009-2614/84/$ 03.00

more adiabatic. A study of pressure-broadening cross sections for this system [7] found that while the IOS approximation was excellent for the lowest rotational line (i.e. $J = 0 - 1$), it became increasingly poorer for higher rotational levels. This is in contrast to CO–He for which the IOS approximation does accurately predict the dependence of pressure-broadening cross sections on going to higher rotational levels.

2. Calculations and results

The CO–Ar potential was obtained within the Gordon and Kim [8] electron gas formalism. Calculations were done at seven orientations, $\theta = 0(30)180$, for the intermolecular separations $R = 3.0(0.5)8.5$ bohr radii. The angular dependence was expanded in terms of Legendre polynomials retaining the five terms through P_4. Continuous radial coefficients in the Legendre expansion were obtained by spline interpolation, exponential extrapolation for small separations, and inverse power extrapolation at large separation [9]. Although the electron gas model has known deficiencies, it has the virtue of providing a reasonably accurate description of the forces important for rotational excitation at a very modest computational cost. An improved electron gas potential for this system has been given by Parker and Pack [10]. It was shown in ref. [7] that the current electron gas potential provides a reasonable description of pressure-broadening cross sections for this system. Of course, for the present study which is designed to test the accuracy of the IOS scattering approximation, the verisimilitude of the potential is not a crucial factor.

IOS calculations were performed at twenty-five collision energies from 25 to 10000 cm^{-1}. Integration over the angle dependence was done with 96-point Gauss quadrature. Rate constants were obtained by numerically integrating cross sections over a Boltzmann distribution of initial kinetic energies. As discussed in our previous paper [6], the interpretation of energy in the IOS method is ambiguous, and there we considered two possibilities. In the first, the IOS energy was taken as the initial energy for downward collisions, i.e.

$$\sigma_{ID}(j \to 0|E_{in}) = (2j+1)^{-1} Q_j(E_{in}) , \quad (1)$$

where Q_j is a generalized IOS cross section as defined by Goldflam et al. [2] and where the subscript stands for *initial* energy for *downward* collisions. The rate $R_{ID}(j \to 0|T)$ is then obtained by integrating over a Boltzmann distribution of collision energies, and the corresponding upward rate, $R_{ID}(0 \to j|T)$, is obtained from the detailed balance relationship,

$$R_{ID}(0 \to j|T) = (2j+1)\, e^{-\Delta E/kT} R_{ID}(j \to 0|T) , \quad (2)$$

where $\Delta E = E_j - E_0 > 0$. In the second interpretation the IOS energy was taken as the *initial* energy for *upward* transitions, i.e.

$$\sigma_{IU}(0 \to j|E_{in}) = Q_j(E_{in}) \quad (3)$$

and the corresponding rate constant, $R_{IU}(0 \to j|T)$ is obtained by integrating over a Boltzmann distribution. (Note that $Q_j(E)$ is generally non-zero even for energies below the threshold for the $0 \to j$ transition.) It is readily shown that

$$R_{IU}(0 \to j|T) = e^{\Delta E/kT} R_{ID}(0 \to j|T) . \quad (4)$$

For CO–He it was found that R_{IU} provided an overestimate and R_{ID} an underestimate for the true rate constant, the error increasing with inelasticity. However, the geometrical average,

$$R_{IA} = (R_{IU} R_{ID})^{1/2} = e^{\Delta E/2kT} R_{ID} , \quad (5)$$

appeared to provide an accurate estimate. It can be shown that R_{IA} is equivalent to interpreting the IOS energy as the average of the energies for upward and downward transitions and including an energy factor that enforces detailed balance and that is symmetrical with respect to upward and downward transitions; in particular,

$$\sigma_{IA}(0 \to j|E_{in}) = Q_j(E_{in} - \tfrac{1}{2}\Delta E)(E_{in} - \tfrac{1}{2}\Delta E)/E_{in} . \quad (6)$$

It has recently been suggested by Chang et al. [11] that it is more appropriate to interpret the IOS energy as the final kinetic energy. For example, taking the IOS energy as the *final* energy for *downward* collisions one identifies

$$\sigma_{FD}(j \to 0|E_{in}) = (2j+1)^{-1} Q_j(E_{in} + \Delta E) , \quad (7)$$

which gives $R_{FD}(j \to 0|T)$ when integrated over a Boltzmann distribution, with $R_{FD}(0 \to j|T)$ obtained from detailed balance, eq. (2). Taking the IOS energy as the *final* energy for *upward* transitions leads to the identification

$$\sigma_{FU}(0 \to j|E_{in}) = Q_j(E_{in} - \Delta E) , \quad (8)$$

which gives $R_{FU}(0 \rightarrow j|T)$ when integrated over a Boltzmann distribution; note that the $Q_j(E)$ are assumed to vanish for negative E. Because the Q_j in the Boltzmann integrals for R_{FD} and R_{FU} refer to different energies, it is not possible to obtain a simple relationship between them analogous to that between R_{ID} and R_{IU} in eq. (4). One can also define an average, R_{FA}, in analogy with R_{IA} in eq. (5).

Classical trajectory calculations were done using standard methods as described in our earlier paper [6]. A total of 20000 trajectories were run, of which 58 were rejected because the collision was not complete in a reasonable number of steps. In all cases the CO initially had no rotational kinetic energy ($j = 0$) and the final rotational state was determined by a binning procedure.

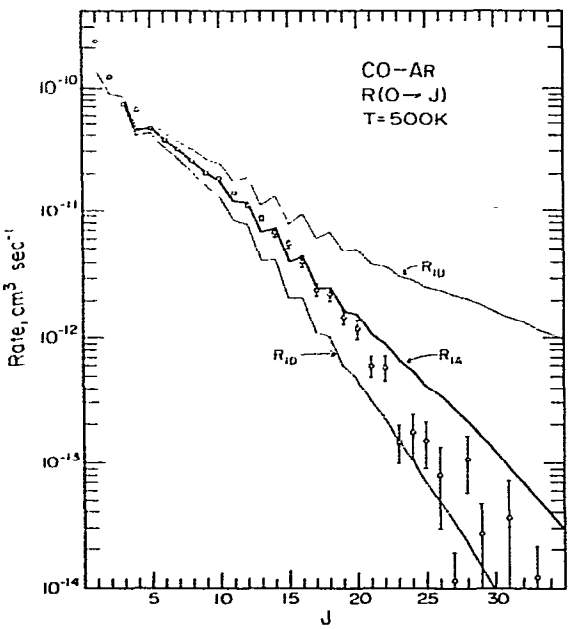

Fig. 1. Comparison of $0 \rightarrow j$ excitation rates in CO–Ar collisions at a kinetic temperature of 500 K. Values from classical trajectory calculations are shown as circles with error bars indicating one sigma uncertainties from the Monte Carlo statistics. Values from IOS calculations are shown as lines. The upper and lower lines assume that the IOS energy is the initial energy for upward and downward collisions, R_{IU} and R_{ID}, respectively. The heavier center line is the geometric average of these, R_{IA}, and is seen to provide good agreement with the classical trajectory values except, perhaps, for very large inelasticity.

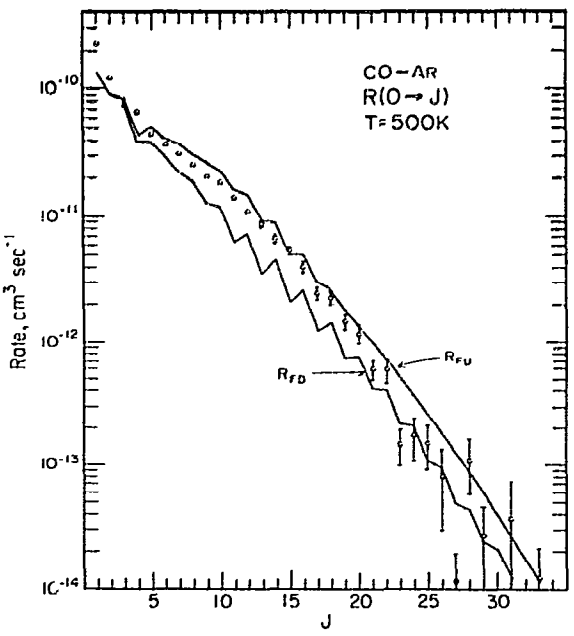

Fig. 2. The same as fig. 1 except that the IOS energy is assumed to be the final kinetic energy for upward and downward collisions, R_{FU} and R_{FD}, respectively.

Results are presented in figs. 1 and 2. Classical trajectory values are indicated by circles with one sigma error bars from the Monte Carlo statistics. IOS values are indicated by lines. In fig. 1 the IOS energy is assumed to be the initial kinetic energy, and R_{IU}, R_{ID}, and R_{IA} are shown. As for CO–He, R_{IU} is too large and R_{ID} is too small, the error increasing with inelasticity. The average, R_{IA}, appears to provide a good estimate, especially when one recalls the shortcomings of classical trajectory values [12], i.e. that $R(0 \rightarrow 1)$ is likely to be too large and that oscillations with final rotational level that come from quantum interference effects are expected to be averaged out. However, for the largest inelasticities shown here ($j > 22$) the classical trajectory values do appear to be significantly lower than R_{IA}, although the satistical uncertainties for these rare events are rather large. A similar, if somewhat less pronounced trend was also observed for CO–He. It seems likely, therefore, that R_{IA} is, in fact, an overestimate of the true rate at high inelasticity. In fig. 2 the IOS energy is assumed to be the final kinetic energy, and R_{FU} and R_{FD} are shown. For small j

these appear to be in poorer agreement with the classical trajectory values than R_{IU} and R_{ID}. The average, R_{FA}, however, is close to R_{IA}. At higher inelasticity R_{FU} and R_{FD} predict smaller rate constants than R_{IA}, giving better agreement with the classical trajectory values. It is particularly noteworthy that interpreting the IOS energy as the final energy gives cross sections that come closer to satisfying detailed balance than do those calculated from an initial energy assumption.

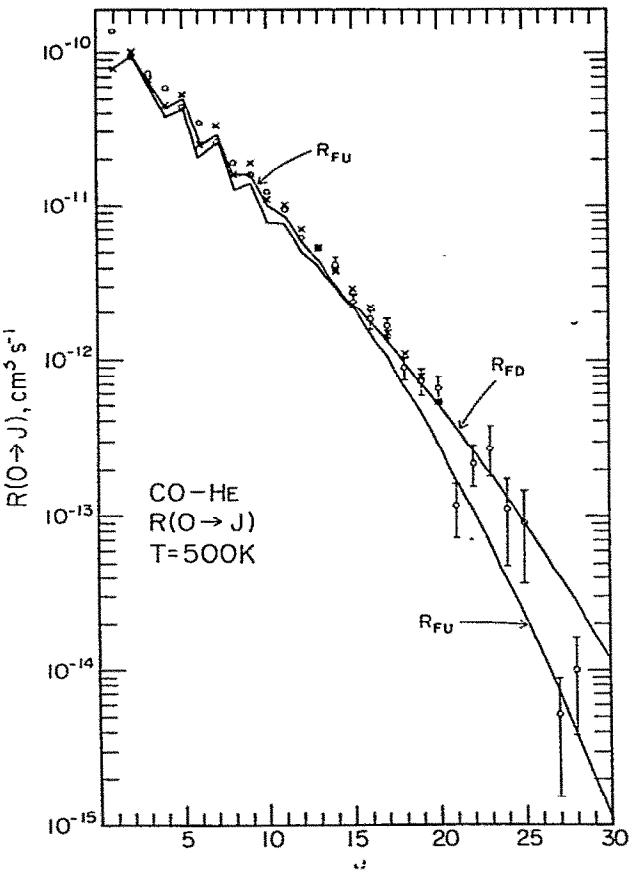

Fig. 3. Comparison of $0\rightarrow j$ excitation rates in CO–He collisions at a kinetic temperature of 500 K. Values from classical trajectory calculations are shown as circles with error bars indicating one sigma uncertainties from the Monte Carlo statistics. Values from coupled states calculations are shown as crosses. Both of these have been reported previously in ref. [6]. Values from IOS calculations are shown as lines. The IOS energy is assumed to be the final kinetic energy for upward and downward collisions, R_{FU} and R_{FD}, respectively.

This is seen graphically by the smaller divergence of R_{FU} and R_{FD} as compared with R_{IU} and R_{ID}, especially for higher inelasticity.

Because the final energy assumption appears to be a better overall choice than the initial energy assumption for this system, we have applied it to CO–He to compare with our earlier results in which only the initial energy assumption was made. Fig. 3 compares IOS R_{FD} and R_{FU} with classical trajectory and coupled states values. As for CO–Ar the final energy assumption gives results that are closer to detailed balance although for larger inelasticity R_{FD} and R_{FU} diverge more for CO–He than for CO–Ar. Interestingly, R_{FD} is larger than R_{FU} here for highly inelastic collisions. Again, as for CO–Ar, the final energy assumption predicts lower rates for highly inelastic collisions, in better agreement with classical trajectory values.

3. Discussion

The accuracy of the IOS approximation for calculating the rates of excitation out of the lowest level, $R(0\rightarrow j)$, in CO–Ar collision has been assessed by comparing with classical trajectory results that are expected to provide an accurate description for this system. As in our previous study of CO–He collisions, it is found that the interpretation of the IOS energy is important. For both systems, good resuls are obtained – at least for small and intermediate inelasticity – by using the average of the initial energies for upward and downward collisions. The recent suggestion that the IOS energy should be interpreted as the final kinetic energy, however, does appear to be a better procedure for both CO–Ar and CO–He; it predicts upward and downward rates that more nearly satisfy detailed balance and it predicts somewhat lower rate constants that are in better accord with classical trajectory values for highly inelastic collisions. Based on our experience with these two systems it appears that R_{FA} provides the best overall estimate for the $0\rightarrow j$ rates and that R_{IA} is also acceptable except, perhaps, for very highly inelastic collisions. While the IOS approximation was expected to be generally excellent for CO–He collisions, it is expected to be less good for CO–Ar collisions owing to the larger reduced mass; and the fact that $R(0\rightarrow j)$ can be calculated accurately for the latter as well as the former is therefore of practical significance.

It has been brought to our attention by an anonymous referee that Sachs and Bowman [13] suggested modifying IOS for vibrational excitation to account symmetrically for both initial and final wavevectors; although their methods are more complicated than our eq. (5), on reanalyzing their results they do not appear to provide greater accuracy. Note that the desirability of using an average collision energy in the IOS method – something along the lines of our eq. (6) – was often discussed among workers in this field; however, we are not aware of any previously published results that actually tested this idea.

References

[1] D.C. Clary, J. Chem. Phys. 75 (1981) 205, 2899; J.M. Bowman and S.C. Leasure, J. Chem. Phys. 66 (1977) 288.
[2] R.Goldflam, S. Green and D.J. Kouri, J. Chem. Phys. 67 (1977) 4149.
[3] A.E. DePristo, S.D. Augustin, R. Ramaswamy and H. Rabitz, J. Chem. Phys. 71 (1979) 850.
[4] T.A. Brunner and D. Pritchard, Advan. Chem. Phys. 50 (1982) 589.
[5] S. Green, Chem. Phys. 31 (1978) 425.
[6] S. Green and S. Chapman, Chem. Phys. Letters 98 (1983) 467.
[7] S. Green, J. Quant. Spectry. Radiative Transfer, to be published.
[8] R.G. Gordon and Y.S. Kim, J. Chem. Phys. 56 (1972) 3122.
[9] S. Green, J. Chem. Phys. 67 (1977) 715.
[10] G.A. Parker and R. T Pack, J. Chem. Phys. 69 (1978) 3268.
[11] B. Chang, L. Eno and H. Rabitz, J. Chem. Phys. 78 (1984) 4477.
[12] S. Chapman and S. Green, J. Chem. Phys. 67 (1977) 2317.
[13] J.G. Sachs and J.M. Bowman, J. Chem. Phys. 73 (1980) 3699.